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(71) Applicant: LIBBEY-OWENS-FORD CO. [US/US]; 811 Madison Avenue, Toledo, OH 43695 (US).			
(72) Inventor: CHENG, J., Joseph ; 309 W. South Boundary, Perrysburg, OH 43551 (US).			
(74) Agent: OBERLIN, Phillip, S.; Marshall & Melhorn, Four SeaGate - 8th Floor, Toledo, OH 43604 (US).			

(54) Title: INFRARED AND ULTRAVIOLET RADIATION ABSORBING GREEN GLASS COMPOSITION

(57) Abstract

Green-colored, infrared energy and ultraviolet radiation absorbing glass compositions comprise conventional soda-lime-silica float glass ingredients, a high concentration of moderately reduced iron, and ceric oxide. The resultant glass exhibits an Illuminant A visible light transmittance greater than 70 %, a total solar energy transmittance less than about 46 %, and an ultraviolet radiation transmittance less than about 38 %, at glass thicknesses in the range of 3 mm to 5 mm. Optionally, a portion of the ceric oxide can be replaced with a predetermined quantity of titanium oxide. Further the glass may be used in an automobile glazing unit comprising two sheets of the glass integrally adhered together through an interposed layer of transparent resinous material such as polyvinyl butyryl.

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CENTRAL FAX CENTERINFRARED AND ULTRAVIOLET RADIATION
ABSORBING GREEN GLASS COMPOSITION

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Field of the Invention

The present invention relates generally to infrared and ultraviolet radiation absorbing green glass compositions, and more specifically to green glass compositions having a particular combination of energy absorption and light transmittance properties. The preferred glass has a narrowly defined dominant wavelength and color purity. The present invention is particularly useful for producing automotive and architectural glazings, wherein high visible light transmittances and low total solar energy and ultraviolet radiation transmittances are desired.

Background of the Invention

It is generally known to manufacture infrared radiation absorbing soda-lime-silica glass by the incorporation therein of iron. The iron is generally present in the glass as both ferrous oxide (FeO) and ferric oxide (Fe₂O₃). The balance between ferrous and ferric oxide has a direct and material effect on the color and transmittance properties of the glass. As the ferrous oxide content is increased (as a result of chemically reducing ferric oxide), the infrared absorption increases and the ultraviolet absorption decreases. The shift toward a higher concentration of FeO in relation to the Fe₂O₃ also causes a change in the color of the glass from a yellow or yellow-green to a darker green or blue-green, which reduces the visible transmittance of the glass. Therefore, in order to obtain greater infrared absorption in glass without sacrificing visual transmittance, it has been deemed necessary in the prior art to produce glass with a low total iron content which is highly reduced from Fe₂O₃ to FeO. A low total iron content glass is generally regarded as one produced from a batch composition

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having less than about .70 to .75% by weight iron calculated as Fe_2O_3 . As an example, U.S. Patent No. 3,652,303 discloses an infrared absorbing blue soda-lime-silica glass composition, having a visible light transmittance greater than 70% at one quarter inch thickness, wherein at least 80% of the total iron in the glass is maintained in the ferrous state by the inclusion of a reducing quantity of tin metal or stannous chloride in the melt.

Many glass compositions additionally contain cerium for the purpose of providing ultraviolet absorption. For example, U.S. Patent No. 1,414,715 discloses the addition of 3% to 6% by weight of ceric oxide to prepare a non-iron-containing glass composition having a flesh tint. The patent additionally teaches that ceric oxide reduces the visible light transmittance of the glass.

U.S. Patent No. 1,637,439 discloses the use of 5% to 10% by weight of ceric oxide as an ultraviolet absorber in dark blue glass compositions. The glass, which is useful for example for observing the operation of an open-hearth furnace, is made dark blue by the addition of 0.1% to 0.5% by weight of cobalt oxide. The high concentration of ceric oxide absorbs virtually all of the ultraviolet radiation which would otherwise pass through the eye protecting glass. Clearly, such a glass composition has a low visible light transmittance, and would not be useful for automotive or architectural glazings.

U.S. Patent No. 1,936,231 discloses a colorless glass, wherein ferric oxide is added as an ultraviolet cut-off agent in quantities so small that the resultant glass retains its high visible light transmittance. The suggested total iron content is approximately 0.35% by weight. The patent further discloses that cerium compounds may be added, as ultraviolet radiation cut-off agents, to low total iron containing glass compositions. Thus, the resultant glass compositions retain their colorless appearance and high visible light transmittance properties.

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U.S. Patent No. 2,524,719 discloses a rose colored glass composition, wherein iron is added to the glass batch as an infrared energy absorber, and selenium is added as an ultraviolet radiation absorber. It is suggested that ceric oxide may be included, at an amount in excess of 3% by weight, to assist the selenium in the absorption of ultraviolet radiation.

U.S. Patent No. 2,860,059 discloses an ultraviolet absorbing glass composition, having a low total iron concentration, which is described as superior in visible light transmittance to the greenish-blue glasses generally used in automotive and architectural glazings. The maximum iron content is 0.6% by weight, in order for the glass to maintain its colorless appearance and high visible light transmittance. Titanium dioxide, and up to 0.5% by weight ceric oxide, are added to the glass for the purpose of providing ultraviolet radiation absorption.

U.S. Patent No. 2,444,976 discloses a golden color glass particularly adapted for glazing aircraft having an exceptionally low transmittance in the ultraviolet and a high transmittance in the visible. The glass contains iron oxide as a heat absorbing component together with large amounts of both cerium oxide (1.5% to 3%) and titanium oxide (6% to 9%).

Finally, U.S. Patent No. 4,792,536 discloses a process for producing an infrared energy absorbing glass, containing a low total iron concentration which is highly reduced to FeO. It is further disclosed that the infrared energy absorption can be increased by including greater amounts of total iron in the glass composition, but states that the visible light transmittance would thereby be reduced below levels considered adequate for automotive glazings. The disclosed process utilizes a two stage melting and refining operation, which provides highly reducing conditions so as to increase the amount of iron in the ferrous state for a given low total iron concentration of from 0.45% to 0.65% by weight. The patent teaches that the iron must be at least

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35% reduced to FeO. Most preferably, greater than 50% of the total iron content must be reduced to the ferrous state. It is further disclosed that 0.25% to 0.5% by weight of ceric oxide may be added to low total concentration, highly reduced 5 iron containing glass compositions, for the purpose of absorbing ultraviolet radiation. It is disclosed that higher concentrations of ceric oxide are to be avoided, as they would compromise the overall transmittance properties of the glass. As an example of the glass which may be produced by 10 the process taught in U.S. Patent No. 4,792,536, Composition No. 11 discloses a low total iron containing glass, which is 30% reduced to FeO, and contains 1% ceric oxide. At a thickness of 4 mm, the total solar energy transmittance is about 52%, and the ultraviolet radiation transmittance is 15 about 37%. The relatively high total solar energy transmittance value results from the low total iron concentration, while the relatively high ultraviolet radiation transmittance value is caused by the low concentration of Fe₂O₃, a large portion of which has been 20 reduced to FeO.

It would be desirable to produce a green-colored glass, utilizing conventional float glass technology, for use in automotive and architectural glazings, having a high Illuminant A visible light transmittance of at least 70%, a 25 low total solar energy transmittance of less than about 46%, and a low ultraviolet radiation transmittance of less than about 38%, at nominal glass thicknesses in the range of 3 mm to 5 mm *. A green glass composition having these outstanding transmittance properties can not be produced 30 utilizing the low total concentration, highly reduced iron

35 * It should be understood that by this recitation of glass thickness is meant total glass thickness, and the glazing unit comprising same may be composed of a single glass sheet or two or more glass sheets, the total thickness of which is in the indicated range.

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containing glass compositions employing ceric oxide as disclosed in the prior art. Moreover, the use of a high total iron containing glass for this purpose is contrary to the teachings of the prior art.

5 It must be noted that the prior art referred to hereinabove has been collected and examined only in light of the present invention as a guide. It is not to be inferred that such diverse art would otherwise be assembled absent the motivation provided by the present invention.

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Summary of the Invention

In accordance with the present invention, a green glass composition, having an Illuminant A visible light transmittance value of at least 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38% and preferably not greater than approximately 34%, at nominal glass thicknesses of 3 to 5 mm, has surprisingly been discovered.* The composition comprises a soda-lime-silica glass including as essential ingredients from about 0.51 to about 0.96 weight percent Fe_2O_3 , from about 0.15 to about 0.33 weight percent FeO , and from about 0.2 to about 1.4 weight percent GeO_2 . Alternatively, the amount of GeO_2 may be reduced by the inclusion of from about 0.02 to about 0.85 weight percent TiO_2 . Percentages of TiO_2 below about .02 weight percent are normally present as trace amounts in soda-lime-silica glasses. These glasses have an Illuminant C dominant wavelength from about 498 to about 525 nanometers, preferably from 498 to 519 nanometers, and a color purity from about 2% to about 4% preferably from about 2% to about 3%. They are

* Radiation transmittance results are based upon the following wavelength ranges:

35	Ultraviolet	300-400	nanometers
	visible	400-770	nanometers
	Total Solar	300-2130	nanometers

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produced from batch compositions having a total iron concentration, expressed as Fe_2O_3 , above about 0.7%. *

The glass compositions of the present invention are particularly suited for the production of infrared energy and ultraviolet radiation absorbing green glass, for automotive and architectural glazings. Thus, glass sheets of this composition may be heat strengthened or tempered; or alternately annealed and laminated together through an interposed transparent resinous layer, for example composed of polyvinyl butyral, and employed, for example, as a windshield. Generally, the glass sheets for windshield use are of a thickness in the range of from about 1.7 mm to about 2.5 mm, while those tempered and used as sidelights or backlights are in the range of about 3 mm to about 5 mm thick.

Unless otherwise noted, the term percent (%) as used herein and in the appended claims, means percent (%) by weight. Wavelength dispersive X-ray fluorescence was used to determine the weight percents of GeO_2 , TiO_2 , and total iron expressed as Fe_2O_3 . Percent reduction of total iron was

* It is common in the glass industry to refer to the total iron contained in a glass composition or batch as "total iron expressed as Fe_2O_3 ". When a glass batch is melted, however, some of this amount of total iron is reduced to FeO , while the rest remains Fe_2O_3 . For this reason, it shall be understood that by " Fe_2O_3 ", as used herein and in the appended claims, is meant weight percent ferric oxide in the glass composition after reduction. By "total iron expressed as Fe_2O_3 " is meant the total weight of iron contained in the glass batch before reduction. Further, when reduced to FeO , Fe_2O_3 will produce not only FeO , but oxygen gas. This loss of oxygen will decrease the combined weight of the two iron compounds. Therefore, the combined weight of FeO and Fe_2O_3 contained in a resulting glass composition will be less than the batch weight of the total iron expressed as Fe_2O_3 .

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determined by first measuring the radiant transmission of a sample at a wavelength of 1060 nanometers, using a spectrophotometer. The 1060 nm transmission value was then used to calculate optical density, using the following 5 formula:

$$\text{Optical density} = \log_{10} \frac{100}{T} \quad (T = \text{transmission at } 1060 \text{ nm}).$$

The optical density was then used to calculate the percent 10 reduction:

$$\text{percent reduction} = \frac{(110) \times (\text{optical density})}{(\text{Glass thickness in mm}) \times (\text{wt\% total Fe}_2\text{O}_3)}$$

Detailed Description of the Preferred Embodiment

15 For use as an automotive windshield, infrared energy and ultraviolet radiation absorbing glass must meet federal specifications which require an Illuminant A visible light transmittance greater than 70%. The thinner glasses used in modern automobiles have made it easier to achieve the 70% 20 Illuminant A standard, but have also resulted in increased infrared energy and ultraviolet radiation transmittances. Consequently, automobile manufacturers have been forced to compensate for greater heat loads by appropriately sizing air 25 conditioning equipment, and are compelled to include more ultraviolet radiation stabilizers in fabrics and interior plastic components in order to prevent their degradation.

The green glass compositions of the present invention, when fabricated to a total glass thickness of about 3 mm to 30 5 mm, can exhibit an Illuminant A visible light transmittance value of at least 70%, and provide combined infrared energy and ultraviolet radiation transmittance values substantially lower than the compositions disclosed in the prior art. The total solar energy transmittance of the compositions of the present invention, at selected glass thicknesses in the range 35 of 3 mm to 5 mm, is less than about 46%. Preferably, the total solar energy transmittance in these thicknesses is less than about 45%. Total solar energy transmittance is a

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measure of the solar energy transmittance over all solar energy wavelengths. It is an integrated term covering the area under the transmittance versus wavelength curve for visible, infrared and ultraviolet energy wavelengths.

5 The ultraviolet radiation transmittance of the compositions of the present invention is less than about 38%, at selected glass thicknesses in the range of 3 mm to 5 mm, and generally not more than about 34%. The ultraviolet radiation transmittance value is an integrated term
10 representing the area under the transmittance versus wavelength curve for wavelengths between 300 and 400 nanometers. The ultraviolet radiation transmittance values for glass compositions of the present inventions were calculated by integrating the Perry Moon air mass 2 solar
15 spectral energy distribution* between 300 and 400 nm, and ratioing the attenuated energy transmitted by the sample over that same spectral region.

Suitable batch materials according to the present invention, which are compounded by conventional glass batch
20 ingredient mixing devices, include sand, limestone, dolomite, soda ash, salt cake or gypsum, rouge, carbon, and a cerium compound such as ceric oxide or cerium carbonate, and optionally a titanium compound such as titanium dioxide. These materials are conveniently melted together in a
25 conventional glass making furnace, to form a green-colored infrared energy and ultraviolet radiation absorbing glass composition, which thereafter may be continuously cast onto the molten metal bath in a float glass process. The flat glass thus produced may be formed into architectural
30 glazings, or cut and formed, such as for example by press bending, into automotive glazings.

35 * From "Proposed Standard Solar-Radiation Curves for Engineering Use", Perry Moon, M.I.T., Journal of the Franklin Institute, No. 230, pp. 583-617 (1940).

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The composition of the resultant soda-lime-silica glass comprises:

- A) from about 65 to about 75 weight percent SiO₂;
- B) from about 10 to about 15 weight percent Na₂O;
- 5 C) from 0 to about 4 weight percent K₂O;
- D) from about 1 to about 5 weight percent MgO;
- E) from about 5 to about 15 weight percent CaO;
- F) from 0 to about 3 weight percent Al₂O₃;
- G) from about 0.51 to about 0.96 weight percent Fe₂O₃;
- 10 H) from about 0.15 to about 0.33 weight percent FeO; and
- I) from about 0.2 to about 1.4 weight percent CeO₂.

Preferably, the resultant glass composition consists essentially of:

- 15 A) from about 70 to about 73 weight percent SiO₂;
- B) from about 12 to about 14 weight percent Na₂O;
- C) from 0 to about 1 weight percent K₂O;
- D) from about 3 to about 4 weight percent MgO;
- E) from about 6 to about 10 weight percent CaO;
- 20 F) from 0 to about 2 weight percent Al₂O₃;
- G) from about 0.51 to about 0.96 weight percent Fe₂O₃;
- H) from about 0.15 to about 0.33 weight percent FeO; and
- I) from about 0.2 to about 1.4 weight percent CeO₂.

25 Alternatively, the quantity of ceric oxide in the glass may be reduced by the inclusion therein of titanium dioxide. In order to maintain the desired ranges of transmittance, dominant wavelength, and color purity described hereinabove, when substituting titanium dioxide for ceric oxide in the 30 glass, the weight percent of total iron expressed as Fe₂O₃ must be reduced, and the percent reduction to FeO must be increased. This results in a glass comprising:

- A) from about 65 to about 75 weight percent SiO₂;
- B) from about 10 to about 15 weight percent Na₂O;

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- C) from 0 to about 4 weight percent K₂O;
- D) from about 1 to about 5 weight percent MgO;
- E) from about 5 to about 15 weight percent CaO;
- F) from 0 to about 3 weight percent Al₂O₃;
- 5 G) from about 0.5 (.48) to about 0.9 (.92) weight percent Fe₂O₃;
- H) from about 0.15 to about 0.33 weight percent FeO;
- I) from about 0.1 to about 1.36 weight percent CeO₂; and
- J) from about 0.02 to about 0.85 weight percent TiO₂.

10

It shall be noted that, at low quantities of TiO₂ inclusion, each weight percent of TiO₂ must replace two weight percent of CeO₂ to maintain the glass properties described hereinabove. As the level of TiO₂ increases, 15 however, the effect of TiO₂ addition lessens slightly. For example, a composition initially containing 1.0 weight percent CeO₂ and no added TiO₂ will require about .3 weight percent TiO₂ to replace about .5 weight percent CeO₂ and still maintain glass properties (thus at higher quantities of 20 TiO₂ substitution, each weight percent TiO₂ will replace about 1.5 weight percent CeO₂). Preferably, the glass composition employing titanium dioxide consists essentially of:

- A) from about 70 to about 73 weight percent SiO₂;
- 25 B) from about 12 to about 14 weight percent Na₂O;
- C) from 0 to about 1 weight percent K₂O;
- D) from about 3 to about 4 weight percent MgO;
- E) from about 6 to about 10 weight percent CaO;
- F) from 0 to about 2 weight percent Al₂O₃;
- 30 G) from about 0.5 (.48) to about 0.9 (.92) weight percent Fe₂O₃;
- H) from about 0.15 to about 0.33 weight percent FeO;
- I) from about 0.1 to about 1.36 weight percent CeO₂; and
- J) from about 0.02 to about 0.85 weight percent TiO₂.

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Silica forms the glass matrix. Sodium oxide, potassium oxide, magnesium oxide, and calcium oxide act as fluxes to reduce the melting temperature of the glass. Alumina regulates the viscosity of the glass, and prevents 5 divitrification. Moreover, the magnesium oxide, calcium oxide, and alumina act together to improve the durability of the glass. Salt cake or gypsum acts as a refining agent, while carbon is a known reducing agent.

Iron is added, typically as Fe_2O_3 , and is partially 10 reduced to FeO . The total amount of iron in the batch is critical, and must equal from 0.7% to about 1.25% by weight, expressed as Fe_2O_3 . Likewise, the degree of reduction is critical and must equal between 23% and 29%. The aforementioned critical ranges, for total iron and the degree 15 of reduction from ferric to ferrous iron, result in concentrations from about 0.51 to about 0.96 weight percent Fe_2O_3 and from about 0.15 to about 0.33 weight percent FeO in the glass. If the iron is more highly reduced than the critical amount, the glass will become too dark and the 20 illuminant A visible light transmittance will drop below 70%. Additionally, the glass batch melting process will become increasingly difficult as the increased amount of FeO prevents the penetration of heat to the interior of the melt. If the iron is less reduced than the critical amount, or if a 25 lower total amount of iron is employed, then the total solar energy transmittance for a desired thickness glass can rise above about 46%. Finally, if an amount of total iron higher than the critical amount is used, less heat will be able to penetrate the interior of the melt, and the batch melting 30 process will become increasingly more difficult. Clearly, the high total iron concentration, and low reduction to FeO , are critical to the performance of the glass, and contrary to the teachings of that prior art directed to glass compositions having a high visible light transmittance and 35 low infrared energy and ultraviolet radiation transmittances.

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Moreover, the concentration of the ceric oxide ultraviolet radiation absorber, in concert with the iron, is critical to the balance of transmittance properties. The ceric oxide must be present at a concentration from about 5 0.2% to about 1.4% by weight. A higher concentration of ceric oxide would absorb more radiation in the 400 to 450 nanometers wavelength range, causing the color of the glass to change from green to yellow-green. A lower concentration of ceric oxide would cause the ultraviolet radiation 10 transmittance to rise above about 38%. A combination of from about 0.1 to about 1.36 weight percent CeO_2 and from about 0.02 to about 0.85 weight percent TiO_2 may be substituted for the aforementioned amount of from about 0.2 to about 1.4 weight percent of ceric oxide alone. The combination of 15 ceric oxide and titanium dioxide have the same operability and utility as the greater required amount of ceric oxide alone, and deviations above or below the stated maximums and minimums for these ingredients will detrimentally affect the absorbence and color properties of the glass as recited 20 hereinabove for ceric oxide alone.

As can be seen, the synergistic effect of the critical concentration limits for the iron and ceric oxide, and the critical limitation for the degree of reduction of Fe_2O_3 to FeO , is to produce a green glass composition having an 25 Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance of less than about 38%, preferably less than about 34%.

Moreover, the green glass of the present invention is 30 characterized by an Illuminant C dominant wavelength from about 498 to about 525 nanometers, and displays a color purity from about 2% to about 4%. The purity of an automotive vision glazing is an important parameter, and should be maintained at as low a level as practicable. Blue 35 glass, by comparison, has a purity of up to about 10%, and therefore is less desirable as an automotive vision glazing.

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As hereinbefore indicated, the invention particularly contemplates and concerns glazings of glass thicknesses in the range of 3 mm to 5 mm. Examples of soda-lime-silica compositions in accordance with the invention at specific thicknesses in this range are set forth below. All of these glasses have Illuminant A visible light transmittances equal to or greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

10

Table I

	<u>Total Weight</u> <u>% in Glass</u>	<u>3 mm</u>	<u>4 mm</u>	<u>5 mm</u>
15	Fe ₂ O ₃	.71 to .95	.54 to .65	.51 to .59
	FeO	.26 to .32	.18 to .22	.14 to .17
	CaO ₂	0.8 to 1.4	.55 to 1.2	0.2 to 0.7
	% Reduction	23 to 29	23 to 29	23 to 29

20

Table II

	<u>Total Weight</u> <u>% in Glass</u>	<u>3 mm</u>	<u>4 mm</u>	<u>5 mm</u>
25	Fe ₂ O ₃	0.68 to 0.92	.51 to .62	.48 to .56
	FeO	0.26 to 0.32	.18 to .22	.14 to .17
	CaO ₂	.5 to 1.2	.3 to .75	.1 to .4
	TiO ₂	.02 to .85	.02 to .45	.02 to .3
	% Reduction	23 to 29	23 to 29	23 to 29

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Examples 1-16

Typical soda-lime-silica glass batch ingredients were mixed, together with rouge, a cerium compound, a carbonaceous reducing agent, and optionally a titanium compound, and melted to produce 4 mm thick test samples in accordance with the invention. The resultant glass samples are characterized as follows:

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Table III
Glass Properties at 4 mm

		<u>Ex. 1</u>	<u>Ex. 2</u>	<u>Ex. 3</u>	<u>Ex. 4</u>	<u>Ex. 5</u>
5	Total Iron, as Fe ₂ O ₃ (%)	.782	.789	.783	.788	.788
10	Reduction of Iron to FeO (%)	25.1	25.7	26.2	27.3	27.5
	Fe ₂ O ₃ (%)	.586	.586	.578	.573	.571
15	FeO (%)	.177	.182	.185	.194	.195
	CaO ₂ (%)	.913	.909	.915	.914	.913
	TiO ₂ (%)	0	0	0	0	0
20	Illuminant A (%) Transmittance	72.8	72.3	72.2	71.2	71.5
	Total Solar Transmittance (%)	45.9	45.1	44.8	43.9	43.7
25	UV Transmittance (%)	33.0	33.2	33.3	33.5	33.5
	Dominant Wavelength (nm)	512.8	509.2	508.2	505.2	504.5
30	Color Purity (%)	2.4	2.4	2.5	2.8	2.9

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Table III (cont.)

Glass Properties at 4 mm

		Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
5	Total Iron, as Fe ₂ O ₃ (%)	.784	.78	.78	.84	.81	.833
10	Reduction of Iron to FeO (%)	27.7	27.4	27.0	25.8	26.7	26.5
15	Fe ₂ O ₃ (%)	.567	.566	.569	.623	.594	.612
20	FeO (%)	.195	.192	.190	.195	.195	.199
25	GeO ₂ (%)	.911	.6	.6	.91	.56	.915
30	TiO ₂ (%)	0	.2	.2	0	.25	.021
35	Illuminant A (%) Transmittance	71.6	70.4	70.2	71.5	71.7	71.3
40	Total Solar Transmittance (%)	43.6	42.9	43.1	43.7	43.8	43.5
45	UV Transmittance (%)	33.6	30.7	30.1	33.2	33.1	33.4
50	Dominant Wavelength (nm)	504.6	507.9	507.6	506.5	514.1	505.8
55	Color Purity (%)	2.9	2.8	2.9	2.6	2.5	2.8

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Table III (cont.)

Glass Properties at 4 mm

		<u>Ex. 12</u>	<u>Ex. 13</u>	<u>Ex. 14</u>	<u>Ex. 15</u>	<u>Ex. 16</u>
5	Total Iron, as Fe ₂ O ₃ (%)	.813	.84	.74	.74	.85
10	Reduction of Iron to FeO (%)	26.7	23.0	24.8	28.8	16.4
15	Fe ₂ O ₃ (%)	.596	.647	.556	.527	.711
20	FeO (%)	.195	.174	.165	.192	.125
25	CaO ₂ (%)	.563	.498	.5	.5	.7
30	TiO ₂ (%)	.253	.25	0	0	0
35	Illuminant A (%) Transmittance	71.7	71.0	74.2	72	74.9
40	Total Solar Transmittance (%)	43.8	45.0	47.8	44.3	51.2
45	UV Transmittance (%)	33.1	33.3	39.4	40.1	28.9
50	Dominant Wavelength (nm)	514.1	519.0	498.6	495.7	550.8
55	Color Purity (%)	2.5	2.4	3.3	4.4	4.1

The complete compositions of the glasses of Exs. 11 and 12 are as follows:

		<u>Ex. 11</u>	<u>Ex. 12</u>
40	SiO ₂	71.58	71.64
	Na ₂ O	13.75	13.97
	CaO	8.42	8.38
	MgO	4.14	3.97
	Fe ₂ O ₃	.833	.813
45	TiO ₂	.021	.253
	Al ₂ O ₃	.12	.16
	SO ₃	.13	.14
	K ₂ O	0	.02
	Cr ₂ O ₃	.0002	.0003
50	CeO ₂	.915	.563
	La ₂ O ₃	.008	.006

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Predictive Examples 17-22

		<u>Ex. 17</u>	<u>Ex. 18</u>	<u>Ex. 19</u>	<u>Ex. 20</u>	<u>Ex. 21</u>	<u>Ex. 22</u>
5	Total Iron, as Fe ₂ O ₃ (%)	.76	.74	.74	.86	.86	.88
10	Reduction of Iron to FeO (%)	23	24	23	25	27	26
15	Fe ₂ O ₃ (%)	.585	.562	.570	.645	.628	.651
20	FeO (%)	.157	.160	.153	.194	.209	.205
25	CeO ₂ (%)	.2	.3	.4	.5	.6	.7
30	TiO ₂ (%)	0	0	0	0	0	0
35	Illuminant A (%)						
40	Transmittance	70.6	70.6	71.2	71.1	70.0	70.1
45	Total Solar Trans- mittance (%)	42.4	42.5	43.3	42.7	41.2	41.1
50	UV Transmit- tance (%)	35.2	35.3	34.1	34.4	35.1	32.0
55	Thickness (mm)	5	5	5	4	4	4

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An automotive windshield in accordance with the invention, comprising two sheets of a green glass composition, namely, 71.73% SiO₂, 13.78% Na₂O, 8.64% CaO, 4.00% MgO, .776% total iron expressed as Fe₂O₃ (which is 24.3% reduced to FeO), trace (.017%) TiO₂, .12% Al₂O₃, .14% SO₃, .0003% Cr₂O₃, .89% CeO₂, and .009% La₂O₃, each sheet having a nominal thickness of 2.2 mm, with an interposed polyvinyl butyral interlayer of nominal .030 inch thickness, has the following properties: Illuminate A transmittance = 71.4 %, total solar transmittance = 43.0 %, UV transmittance = 16.3 %, dominant wavelength = 518.6 nm, and color purity = 2.5 %.

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A similar automotive windshield in accordance with the invention, consisting of two sheets of a green glass composition including .834% total iron expressed as Fe_2O_3 (which is 26.8% reduced to FeO), trace (.016%) TiO_2 , and .913% GeO_2 , each sheet having a nominal thickness of 1.8 mm, with an interposed polyvinyl butyral interlayer of nominal .030 thickness, has the following properties: Illuminate A transmittance = 72.2%, total solar transmittance = 44.1%, UV transmittance = 17.1%, dominant wavelength = 511 nm, and color purity = 2.4%.

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WHAT IS CLAIMED IS:

1. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from 0.51 to about 0.96 weight percent Fe_2O_3 , from about 0.15 to about 0.33 weight percent FeO , and from about 0.2 to about 1.4 weight percent CaO_2 .
2. A green-colored glass as defined in claim 1, wherein said weight percent FeO represents a percent reduction of total iron, expressed as Fe_2O_3 , of 23% to 29%.
3. A green-colored glass as defined in claim 1, wherein the Illuminant C dominant wavelength is from about 498 to 525 nanometers, and the color purity is from about 2% to about 4%.
4. A green-colored glass as defined in claim 3, wherein said glass at a thickness in the range of from about 3 mm to about 5 mm has an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38%.
5. A green-colored glass as defined in claim 4, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, the total solar energy transmittance is less than about 45%, and the ultraviolet radiation transmittance is not greater than about 34%.
- 30 6. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from .48 to about .92 weight percent Fe_2O_3 , from about 0.15 to about 0.33 weight percent FeO , from about 0.1 to about 1.36 weight percent CaO_2 , and from about 0.02 to about 0.85 weight percent TiO_2 .

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7. A green-colored glass according to claim 6, wherein the Illuminant C dominant wavelength is from about 498 to 525 nanometers, and the color purity is from about 2% to about 4%.

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8. A green-colored glass as defined in claim 7, wherein said glass at a thickness in the range of from about 3 mm to about 5 mm has an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38%.

9. A green-colored glass as defined in claim 8, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, the total solar energy transmittance is less than about 45%, and the ultraviolet radiation transmittance is not greater than about 34%.

20 10. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about 0.54 to about 0.65 weight percent Fe_2O_3 , from about 0.18 to about 0.22 weight percent FeO , and from about 0.55 to about 1.2 weight percent CeO_2 ,
25 said glass at a nominal thickness of 4 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

30 11. A green-colored soda-lime-silica glass as defined in claim 10, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

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12. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about 0.71 to about 0.95 weight percent Fe_2O_3 , from about 0.26 to about 0.32 weight percent 5 FeO , and from about 0.8 to about 1.4 weight percent CaO_2 , said glass at a nominal thickness of 3 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

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13. A green-colored soda-lime-silica glass as defined in claim 12, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, and the ultraviolet radiation 15 transmittance is not greater than about 34%.

14. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about 0.51 to about 0.59 weight 20 percent Fe_2O_3 , from about 0.14 to about 0.17 weight percent FeO , and from about 0.2 to about 0.7 weight percent CaO_2 , said glass at a nominal thickness of 5 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an 25 ultraviolet radiation transmittance less than about 36%.

15. A green-colored soda-lime-silica glass as defined in claim 14, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is 30 from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

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16. A green-colored, infrared energy and ultraviolet radiation absorbing glass composition, comprising:

- A) from about 65 to about 75 weight percent SiO_2 ;
- B) from about 10 to about 15 weight percent Na_2O ;
- 5 C) from 0 to about 4% weight percent K_2O ;
- D) from about 1 to about 5 weight percent MgO ;
- E) from about 5 to about 15 weight percent CaO ;
- F) from 0 to about 3 weight percent Al_2O_3 ;
- G) from about 0.53 to about 0.96 weight percent
- 10 Fe_2O_3 ;
- H) from about 0.15 to about 0.33 weight percent FeO ;
- and
- I) from about 0.2 to about 1.4 weight percent CaO_2 .

15 17. A green-colored glass composition as defined in claim 16, wherein at thicknesses in the range of 3 mm to 5 mm the Illuminant A visible light transmittance is greater than 70%, the total solar energy transmittance is less than about 46%, the ultraviolet radiation transmittance is less than 20 about 38%, the Illuminant C dominant wavelength is from about 498 to about 525 nanometers, and the color purity is from about 2% to about 4%.

18. A green-colored, infrared energy and ultraviolet 25 radiation absorbing glass composition, consisting essentially of:

- A) from about 70 to about 73 weight percent SiO_2 ;
- B) from about 12 to about 14 weight percent Na_2O ;
- C) from 0 to about 1 weight percent K_2O ;
- 30 D) from about 3 to about 4 weight percent MgO ;
- E) from about 6 to about 10 weight percent CaO ;
- F) from 0 to about 2 weight percent Al_2O_3 ;
- G) from about 0.53 to about 0.96 weight percent
- Fe_2O_3 ;

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H) from about 0.15 to about 0.33 weight percent FeO;
and

I) from about 0.2 to about 1.4 weight percent CeO₂.

5 19. A green-colored glass composition as defined in
claim 18, wherein at thicknesses in the range of 3 mm to 5 mm
the Illuminant A visible light transmittance is greater than
70%, the total solar energy transmittance is less than about
10 46%, the ultraviolet radiation transmittance is less than
about 38%, the Illuminant C dominant wavelength is from about
498 to about 525 nanometers, and the color purity is from
about 2% to about 4%.

20. A green-colored, infrared energy and ultraviolet
15 radiation absorbing soda-lime-silica glass including as
essential ingredients from about .51 to about .62 weight
percent Fe₂O₃, from about .18 to about .22 weight percent
FeO, from about .3 to about .75 weight percent CeO₂, and
about .02 to about .45 weight percent TiO₂, said glass at a
20 nominal thickness of 4 mm having an Illuminant A visible
light transmittance greater than 70%, a total solar energy
transmittance less than about 46%, and an ultraviolet
radiation transmittance less than about 36%.

25 21. A green-colored soda-lime-silica glass as defined
in claim 20, wherein the Illuminant C dominant wavelength is
from about 498 to about 518 nanometers, the color purity is
from about 2% to about 3%, and the ultraviolet radiation
transmittance is not greater than about 34%.

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22. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about .48 to about .56 weight % Fe_2O_3 , from about .14 to about .17 weight percent FeO , from 5 about .1 to about .4 weight percent CeO_2 , and about .02 to about .35 weight percent TiO_2 , said glass at a nominal thickness of 5 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet 10 radiation transmittance less than about 36%.

23. A green-colored soda-lime-silica glass as defined in claim 22, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is 15 from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

24. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as 20 essential ingredients from about .68 to about .92 weight percent Fe_2O_3 , from about .25 to about .32 weight percent FeO , from about .5 to about 1.2 weight percent CeO_2 , and about .02 to about .85 weight percent TiO_2 , said glass at a nominal thickness of 3 mm having an Illuminant A visible 25 light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

25. A green-colored soda-lime-silica glass as defined 30 in claim 24, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

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26. A green-colored, infrared energy and ultraviolet radiation absorbing glass composition, comprising:

- A) from about 65 to about 75 weight percent SiO_2 ;
- B) from about 10 to about 15 weight percent Na_2O ;
- 5 C) from 0 to about 4% weight percent K_2O ;
- D) from about 1 to about 5 weight percent MgO ;
- E) from about 5 to about 15 weight percent CaO ;
- F) from 0 to about 3 weight percent Al_2O_3 ;
- G) from about 0.5 to about 0.9 weight percent Fe_2O_3 ;
- 10 H) from about 0.15 to about 0.33 weight percent FeO ;
- I) from about 0.1 to about 1.36 weight percent CeO_2 ;
- and
- J) from about 0.02 to about 0.85 weight percent TiO_2 .

15 27. A green-colored glass composition as defined in claim 26, wherein at thicknesses in the range of 3 mm to 5 mm the Illuminant A visible light transmittance is greater than 70%, the total solar energy transmittance is less than about 46%, the ultraviolet radiation transmittance is less than about 38%, the Illuminant C dominant wavelength is from about 498 to about 525 nanometers, and the color purity is from about 2% to about 4%.

28. A green-colored, infrared energy and ultraviolet 25 radiation absorbing glass composition, consisting essentially of:

- A) from about 70 to about 73 weight percent SiO_2 ;
- B) from about 12 to about 14 weight percent Na_2O ;
- C) from 0 to about 1 weight percent K_2O ;
- 30 D) from about 3 to about 4 weight percent MgO ;
- E) from about 6 to about 10 weight percent CaO ;
- F) from 0 to about 2 weight percent Al_2O_3 ;
- G) from about 0.5 to about 0.9 weight percent Fe_2O_3 ;
- H) from about 0.15 to about 0.33 weight percent FeO ;

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I) from about 0.1 to about 1.36 weight percent CeO_2 ;
and
J) from about 0.02 to about 0.85 weight percent TiO_2 .

5 29. A green-colored glass composition as defined in
claim 28, wherein at thicknesses in the range of 3 mm to 5 mm
the Illuminant A visible light transmittance is greater than
70%, the total solar energy transmittance is less than about
46%, the ultraviolet radiation transmittance is less than
10 about 38%, the Illuminant C dominant wavelength is from about
498 to about 525 nanometers, and the color purity is from
about 2% to about 4%.

30. An automotive glazing, comprising a green-colored
15 soda-lime-silica glass containing a high total iron
concentration, ceric oxide, and optionally titanium dioxide,
said glazing at a thickness in the range of 3 mm to 5 mm
having an Illuminant A visible light transmittance greater
than 70%, a total solar energy transmittance less than about
20 46%, and an ultraviolet radiation transmittance less than
about 38%.

31. An automotive glazing as defined in claim 30,
having a nominal thickness of 3 mm, an ultraviolet radiation
25 transmittance less than about 36%, an Illuminant C dominant
wavelength from about 498 to about 518 nanometers, and a
color purity from about 2% to 3%.

32. An automotive glazing as defined in claim 31,
30 having an ultraviolet radiation transmittance not greater
than about 34%.

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33. An automotive glazing as defined in claim 30, having a nominal thickness of 4 mm, an ultraviolet radiation transmittance less than about 36%, an Illuminant C dominant wavelength from about 498 to about 518 nanometers, and a 5 color purity from about 2% to 3%.

34. An automotive glazing as defined in claim 30, having a nominal thickness of 5 mm, an ultraviolet radiation transmittance less than about 36%, an Illuminant C dominant 10 wavelength from about 498 to about 518 nanometers, and a color purity from about 2% to 3%.

35. The automotive glazing according to claim 30, wherein said glass is a tempered or heat strengthened float 15 glass sheet.

36. An automotive glazing unit, comprising two sheets of a green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass integrally adhered together 20 through an interposed layer of transparent resinous material, said glass including as essential ingredients from 0.53 to about 0.96 weight percent Fe_2O_3 , from about 0.15 to about 0.33 weight percent FeO , and from about 0.2 to about 1.4 weight percent CeO_2 , said glazing unit having an Illuminant A 25 visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38%.

37. An automotive glazing unit according to claim 36, 30 wherein each of said glass sheets has a thickness in the range of from about 1.7 mm to 2.5 mm.

38. An automotive glazing unit according to claim 37, wherein said transparent resinous material is polyvinyl 35 butyral.

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39. An automotive glazing unit according to claim 38, wherein said polyvinyl butyral layer is about 0.30 inch in thickness.

5 40. An automotive glazing unit according to claim 39, wherein the Illuminant C dominant wavelength of the unit is from about 498 to 530 nanometers, and the color purity is from about 28 to about 48.

10 41. An automotive glazing unit, comprising two sheets of a green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass integrally adhered together through an interposed layer of transparent resinous material, said glass including as essential ingredients from about 0.5 to about 0.9 weight percent Fe_2O_3 , from about 0.15 to about 0.33 weight percent FeO , from about 0.1 to about 1.36 weight percent CeO_2 , and from about 0.02 to about 0.85 weight percent TiO_2 , said glazing unit having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38%.

25 42. An automotive glazing unit according to claim 41, wherein each of said glass sheets has a thickness in the range of from about 1.7 mm to 2.5 mm.

43. An automotive glazing unit according to claim 42, wherein said transparent resinous material is polyvinyl butyral.

30 44. An automotive glazing unit according to claim 43, wherein said polyvinyl butyral layer is about 0.30 inch in thickness.

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45. An automotive glazing unit according to claim 44, wherein the Illuminant C dominant wavelength of the unit is from about 498 to 530 nanometers, and the color purity is from about 2% to about 4%.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/06587

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ^a

According to International Patent Classification (IPC) or to both National Classification and IPC
 INT CL(5): C03C 3/087, 3/095, 4/08; B32B 17/10, 27/42
 U.S. CL.: 501/64, 70, 905

II. FIELDS SEARCHED

Classification System	Minimum Documentation Searched ^a	Classification Symbols
U.S	428/337, 339, 426, 437 501/64, 70, 905	

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ^b

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category ^c	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁶	Relevant to Claim No. ¹⁸
Y	US, A, 4,101,705 (FISCHER ET AL) 18 July 1978 See column 2, lines 29-37 and Examples V and VI.	30-45
Y	US, A, 4,190,452 (FISCHER ET AL) 26 February 1980 See column 2, lines 32-40 and Examples V and VI.	30-45
Y	US, A, 4,701,425 (BAKER ET AL) 20 October 1987 See column 2, lines 31-56.	1-35
X Y	US, A, 4,792,536 (PECORARS ET AL) 20 December 1988 See column 5, lines 10-29 and column 10 lines 44-57	1-36 36-45

- Special categories of cited documents: ¹⁵
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹⁷

10 JANUARY 1991

Date of Mailing of this International Search Report ¹⁸

04 FEB 1991

International Searching Authority ¹⁹

ISA/US

Signature of Authorized Officer ²⁰

MARK BELL